Radiation-Induced Reactions with Cellulose. II. The Trommsdorff Effect: Dose and Dose Rate Studies Involving Copolymerization with Monomers in Methanol

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Synopsis

The radiation-induced grafting to cellulose of styrene, methyl methacrylate, vinyl acetate, 2-vinylpyridine, and 4-vinylpyridine in methanol has been studied. All monomers exhibit appreciable grafting at room temperature in either vacuum or air for total doses up to 10 Mrad and at dose rates as high as 1.4 Mrad/hr. in a spent fuel or ^{60}Co facility. The magnitude of the grafting depends upon both the total dose and dose rate. Under certain experimental conditions, the grafting experiences a maximum which has been attributed to the Trommsdorff effect. A novel mechanism involving charge-transfer bond formation is proposed to account for the observed data in the grafting reactions.

INTRODUCTION

An extensive study has been undertaken of the important factors governing radiation-induced copolymerization of monomers to cellulose. In this, the second of a series of papers, the results deal exclusively with the use of methanol as the solvent in the simultaneous irradiation procedures for grafting with the monomers styrene, methyl methacrylate, vinyl acetate, 2-vinylpyridine, and 4-vinylpyridine in systems of the type cellulose–monomer–methanol.

Since the initiation of this work, a large volume of literature dealing with grafting to cellulose has accumulated but little work has been reported for similar systems. In some instances a fourth component, water, has been included in varying proportions. Generally, the effect of methanol seems to favor grafting. Thus, Arthur and Blouin[1] found that the addition of 1–2% methanol to styrene markedly increased the grafting (or "radiochemical") yield. Demint et al.[2] reiterated these findings and showed, furthermore, that for low styrene concentrations (less than 40–50%), methanol was more effective than dimethylformamide. Usmanov[3,4] recognized in early work that polar, cellulose-wetting solvents, including the alcohols, were conducive to successful grafting with acrylonitrile. Arifov et al.[5] made a limited examination of grafting in dry methanol with styrene, methyl methacrylate, and vinyl acetate. Okamura et al.[6] over-

came the limitation of restricted swelling which confined grafting to the surface of the cellulose fibers by preswelling in a formamide–methanol solution before grafting in styrene–methanol mixtures. No independent evaluation of grafting in methanolic solutions in the absence of the swelling agent has been given. Huang and Rapson[7] studied the effect of methanol in the grafting of styrene to cellulose in the form of rayon and cotton. In some instances, water was used to preswell the fiber but the data covered a limited dose range at a high dose rate (1.27–1.44 Mrad/hr.). The results indicated that in the absence of water, no grafting occurred, whereas small quantities of water sufficed to cause substantial grafting. In further work, Suzuki and Ogawa[8] observed the acceleration of grafting to rayon, in air, in the presence of certain reducing cations. For this purpose, styrene–methanol solutions (1:1) were used.

In contrast, the monomer acrylonitrile may require the presence of water in the grafting system. Saunders and Sovish,[9] concerned primarily with acrylonitrile, failed to observe grafting to cotton in dry methanol (and ethanol) whereas water–methanol (1:1) and aqueous solutions of the monomer gave pick-ups of 8–10%. The same solvent mixture was used for styrene, ethyl acrylate, and methyl methacrylate. Orszagh et al.[10] used methanol and methanol–water mixtures for studying grafting of acrylonitrile, although rather low monomer concentrations were employed (5, 10, and 20%). The best results were obtained with aqueous solutions of acrylonitrile but were limited to a maximum solubility of 7%. Further examination of the methanol–water system showed that maximum yields were obtained for 66% water–33% methanol–20% acrylonitrile. More recently, Hachihama and Sumitomo[11] investigated grafting in a similar system based on cellulose triacetate.

In this paper, grafting in air and vacuum with the five monomers is reported for a wide range of total radiation doses and dose rates at room temperature. A maximum in the grafting yield is discussed together with a novel mechanism involving charge-transfer bond formation to account for certain observations in the grafting reactions.

EXPERIMENTAL

All chemicals were of high purity. However, where necessary further purification was effected either by recrystallization or redistillation. Commercial styrene and vinyl acetate were donated by Monsanto (Aust.) Ltd., and C.S.R. Chemicals Pty. Ltd., respectively; methyl methacrylate, vinylpyridines, acrylic acid, acrylamide, and acrylonitrile were obtained from Lights Ltd.

Preparation of Monomers and Solvent

Liquid monomers were washed with dilute aqueous sodium hydroxide and with water, dried with anhydrous calcium chloride, potassium carbonate, or magnesium sulfate, and distilled under vacuum so that the boiling point

was as low as possible.   For the common monomers, this temperature did not exceed 35°C. and was frequently lower.   Only middle fractions boiling at constant temperature were collected and stored in tightly stoppered, dark bottles in a refrigerator at −2°C.

Methanol was dried by repeated additions of small amounts of anhydrous magnesium sulfate and quicklime.   The dried alcohol was doubly distilled through an efficient column and the distillate stored in dark, tightly stoppered containers.   No attempt was made to prepare extremely dry alcohols due to the limitations imposed in later stages of their use.

Radiation Facilities

Initial experiments were carried out by use of the spent fuel element source of the Australian Atomic Energy Commission's HIFAR reactor (Sydney); later experiments used only ^{60}Co sources. In either case, the facility was of the pond-type, with the radioactive isotope mounted peripherally to form a cylinder of 12–15 in. diameter.   From the radiation flux contour a central region of 7–10 in. diameter within this cylindrical volume was chosen for positioning the materials to be irradiated for maximum uniformity of dose.

In some runs, particularly those requiring very high dose rates, a large cobalt source of 600,000 curies was used (Gamma Sterilization Pty. Ltd., Melbourne).   The geometry of this source was entirely different from the above and suffered from the disadvantage that dose rates decreased rapidly over relatively short distances.   The assembly of the cobalt rods in this case was in a rectangular frame, approximately 5 × 12 ft., and during irradiations the frame was raised from the pond.   With this source, the samples to be irradiated stood within the cell at distances indicated by the predetermined dose-rate measurements.

Dose Rates

The dose rates used ranged from several thousand rads per hour to 1.4 Mrad/hr.   To study the effect of dose rate, this range was investigated at intervals of about 0.2–0.3 Mrad/hr., but for the greater part, the dose rate employed was less than 0.15 Mrad/hr. and depended upon the amount of ^{60}Co available at the time.   For dose rates below 0.02 Mrad/hr., spent fuel element sources were employed.   In all experiments, the dose rates were measured by the ferrous sulfate dosimeter assuming $G_{Fe} = 15.6$, the variation in total dose being quoted as ±5%.

Monomer Solutions

Solutions of monomers were prepared immediately before use wherever possible.   Otherwise, the solutions were held at −2°C. in a desiccator cabinet until required.   The normal monomer concentrations studied were 20, 40, 60, and 80% by volume in each solvent.   The charge of each

solution was maintained constant (6 ml. at room temperature) for all experiments and was placed in the tubes with a minimum of delay and exposure to atmospheric moisture.

Cellulose

In all experiments, cellulose in the form of small strips ($2 \times 1^1/_2$ in) of Whatman No. 41 chromatography paper was used. Without direct handling at any stage, the strips were randomized, numbered, equilibrated at 65% R.H. for 24 hr., and weighed. Finally, the strips were rolled and placed in clean, dry glass tubes (approximately 15 cm. long, 1.2 cm. diameter and 0.1 cm. wall thickness), and stored at constant relative humidity (65%) before filling with the appropriate monomer solution.

Irradiation

The sealed glass tubes (6–8 in. in length) were randomized and assembled in small packages of 3–4 in. diameter or arranged in the form of an annulus of tubes 1–2 in. thick before being positioned in the container. With such an arrangement, it was possible to irradiate 150–200 tubes simultaneously without difficulty. No allowance was made for absorption of the radiation by the mass of packaged glass tubes in either of these procedures since this factor was estimated to be negligible. For irradiations in vacuum, the tubes were subjected to three freeze–thaw cycles and sealed off at less than 10^{-3} cm. Hg pressure by employing a high capacity vacuum system. Following preparation, all tubes were refrigerated at $-2°C.$ before irradiation. Adequate time was allowed for the equilibration of the contents prior to commencing the irradiation.

The samples were placed inside leakproof, aluminum containers (approximately 3 ft. long and 7–12 in. in diameter) in positions conforming to the predetermined dose rate and lowered into the source. The container was rotated through 180° when one half of the full irradiation time had expired.

Extraction

To minimize post-irradiation effects, extraction of strips was started as soon as possible after completion of the irradiation, usually within 2–3 hr. The strips were removed from the tubes with any adhering homopolymer and subjected to continuous extraction in a large Soxhlet extractor for an uninterrupted period of not less than 100 hr. By insulating the extractor from its surroundings, the refluxing solvent reached equilibrium at a temperature in excess of the room temperature. Thus, with benzene the most useful solvent, the equilibrium temperature was 60–65°C.

The solvents, benzene and chloroform, were used for the homopolymers of styrene, methyl methacrylate, vinyl acetate, 2-vinylpyridine, and 4-vinylpyridine. In fact, chloroform was used to establish the completion

of the extraction only and offered no advantages.   After the clean-up with benzene, the extraction of the polyvinylpyridines was completed with methanol.   Otherwise, the extracted strips were rinsed two or three times with ethanol to remove surplus benzene, drained, and dried in an air oven at 60–65°C. for 24–48 hr.   The strips were equilibrated at 65% R.H. for 24 hr. before weighing.

The grafting yield was expressed as the percentage increase in weight of the cellulose strip.   Since prolonged extraction beyond 100 hr. failed to affect the weight gain, the yield was assumed to be a measure of direct grafting to the cellulose backbone polymer.   Reproducibility of grafting yields was usually better than ±5%.

RESULTS AND DISCUSSION

A summary of the simultaneous grafting results obtained for a variety of monomers in methanol is shown in Tables I–V. Preliminary experiments involving the simultaneous grafting of styrene to preirradiated cellulose are included in Table VI.   Methanol has been used as solvent in all of these runs for the reasons which will be discussed in detail in a later paper of this series where the role of solvent in radiation grafting is evaluated.*

Significant features of the results are (1) appreciable grafting can be achieved with all of the above monomers when irradiated in methanol in the presence of cellulose; (2) the magnitude of the grafting is dependent upon the dose rate and the total radiation dose; (3) under certain conditions, the grafting experiences a maximum which may be explained by invoking the Trommsdorff effect; (4) simultaneous irradiation possesses certain advantages over the preirradiation technique.

Comparison of Monomers

Data in Tables I–IV show that styrene, methyl methacrylate, 2- and 4-vinylpyridine, and vinyl acetate, when dissolved in methanol, are all capable of readily grafting to cellulose under the influence of γ-radiation. Preliminary experiments indicate that in both air and vacuum irradiations styrene and methyl methacrylate are the most efficient in the series whereas vinyl acetate is relatively poor.   Methanol is a particularly attractive solvent for this work.   The production of extensive grafting in this alcohol may be related to several phenomena.   Firstly, methanol not only possesses a swelling power approaching that of water but also has the added advantage of being miscible in all proportions with the monomers used. Thus, the problems of access and diffusion are simplified.   However, this situation changes during the course of the irradiation and the increasing volume of the grafting (or grafted) polymer may assist the process of swelling or breaking up of the cellulose structure.   The typical behavior

* It will be observed that water has been excluded in these experiments to the limitations of the practical procedure adopted.

TABLE I
Grafting with Styrene in Methanol Solutions

Dose rate, Mrad/hr.	Dose, Mrad	Atmosphere	Grafting yields at various monomer concentrations, %			
			20 vol.-%	40 vol.-%	60 vol.-%	80 vol.-%
0.100	1	Vacuum	52	105	102	94
		Air	51	123	91	98
	5	Vacuum	69	109	173	220
		Air	76	113	184	250
	10	Vacuum	61	121	166	247
		Air	66	115	179	231
0.140	1	Vacuum	40	68	59	56
		Air	30	65	56	70
	5	Vacuum	55	81	147	209
		Air	54	96	153	229
	10	Vacuum	59	117	161	205
		Air	55	119	171	226
0.250	1	Vacuum	19	47	49	60
		Air	20	49	61	68
	5	Vacuum	47	89	107	144
		Air	52	85	115	155
	10	Vacuum	49	83	148	198
		Air	55	90	143	193
0.390	1	Vacuum	3	10	17	26
		Air	3	10	17	20
	5	Vacuum	26	60	70	91
		Air	30	65	74	110
	10	Vacuum	42	79	135	200
		Air	45	84	136	197
0.412	1	Vacuum	10	25	37	44
		Air	8	21	37	40
	5	Vacuum	26	67	88	104
		Air	27	68	87	108
	10	Vacuum	34	72	120	202
		Air	40	78	127	174

(continued)

observed when extensive grafting occurs supports this hypothesis and the marked swelling weakens the cellulose strip to such an extent that the entire mass readily disintegrates if brought into contact with certain organic liquids.   A second important advantage of methanol is that solvent radicals from the primary radiation act may cause activation of the trunk polymer.

For Table I as a typical example, it can be seen that the grafting rates generally show, as predicted kinetically, that a regular increase occurs with increasing monomer concentration.   At larger radiation doses, a reduction in grafting rates is observed, and this would appear to be associated with the consumption of the monomer and the question of monomer diffusion to an active site.   The latter point may be demonstrated by the post-

TABLE I (*continued*)

Dose rate, Mrad/hr.	Dose, Mrad	Atmosphere	Grafting yields at various monomer concentrations, %			
			20 vol.-%	40 vol.-%	60 vol.-%	80 vol.-%
0.474	1	Vacuum	5	20	36	46
		Air	7	17	23	34
	5	Vacuum	38	76	89	115
		Air	39	75	90	116
	10	Vacuum	42	94	150	221
		Air	47	72	143	207
0.500	1	Vacuum	10	22	41	58
		Air	9	21	40	55
	5	Vacuum	24	61	76	89
		Air	24	51	68	100
	10	Vacuum	40	57	130	169
		Air	44	76	159	201
0.668	1	Vacuum	5	18	29	40
		Air	4	13	23	30
	5	Vacuum	22	54	66	79
		Air	26	55	64	82
	10	Vacuum	30	66	127	172
		Air	33	64	122	171
0.750	1	Vacuum	7	17	39	48
		Air	6	16	29	50
	5	Vacuum	14	37	53	69
		Air	17	42	55	76
	10	Vacuum	32	69	100	108
		Air	35	73	81	107
1.00	1	Vacuum	4	13	29	38
		Air	3	10	16	32
	5	Vacuum	12	30	47	63
		Air	15	34	51	68
	10	Vacuum	31	70	80	105
		Air	32	57	85	101

irradiation effect (Table VII, run 3), where significant increases in grafting are observed if the irradiation is stopped and the tubes are allowed to stand at room temperatures for 170 hr. prior to solvent extraction.

Radiation Dose Effect

In the present experiments, total radiation doses up to 10 Mrad were used. At this level, the radiation damage to the cellulose molecule is considerable[12-14] and, although the grafting yield may be large in both vacuum and air (Tables I, III, IV, and VI) extensive crosslinking can also occur. This crosslinking, which is perhaps the only result with vinyl acetate (Tables III and IV) and 2-vinylpyridine (Table V) at high concentrations (80% by volume), can be particularly troublesome due to the formation of insoluble polymers. Alternatively, when the grafting yield is

high, the strength of the copolymer strip falls markedly,[15] although the total dose may be quite low.

Large radiation doses thus impose detrimental physical limitations on the present system, particularly crosslinking and degradation. By contrast, under suitable experimental conditions, low radiation doses do not suffer from these disadvantages. In this respect, styrene is a particularly attractive monomer, as the results in Table I show. A most important aspect

TABLE II

Grafting of Methyl Methacrylate in Methanol

Dose rate, Mrad/hr.	Dose, Mrad	Atmosphere	Grafting yields at various monomer concentrations, %			
			20 vol.-%	40 vol.-%	60 vol.-%	80 vol.-%
0.1	0.25	Vacuum	66	129	—	148
		Air	56	—	—	147
	0.5	Vacuum	68	—	Lost[a]	Lost
		Air	71	108	Lost	Lost
	1.0	Vacuum	33	—	Lost	Lost
		Air	47	—	Lost	Lost
0.25	0.25	Vacuum	34	78	93	64
		Air	11	23	30	47
	0.5	Vacuum	44	67	80	96
		Air	51	67	—	75
	1.0	Vacuum	52	74	109	68
		Air	66	92	—	68
0.5	0.25	Vacuum	40	68	77	69
		Air	14	38	39	40
	0.50	Vacuum	45	70	78	71
		Air	49	62	—	85
	1.0	Vacuum	54	61	68	75
		Air	39	64	67	56
0.75	0.25	Vacuum	40	69	73	79
		Air	10	29	21	18
	0.5	Vacuum	60	71	84	88
		Air	44	56	61	56
	1.0	Vacuum	43	61	66	66
		Air	55	56	69	60
0.796	0.5	Vacuum	57	109	145	—
		Air	86	129	—	139
1.40	1.0	Vacuum	59	109	143	103
		Air	66	118	177	232

[a] Strips were sometimes "lost" due to the insolubility of associated homopolymer.

of these data (Table I, Fig. 1) at radiation doses of 1 Mrad is the observation that the grafting yield passes through a maximum value at sufficiently low dose rates, i.e., at 0.1 and 0.14 Mrad/hr. This phenomenon may be explained by invoking the Trommsdorff or "gel" effect[16] which functions as the viscosity of the medium increases or precipitation of the polymer occurs.

TABLE III
Grafting Yields for Styrene, Methyl Methacrylate
and Vinyl Acetate in Methanol

Monomer	Dose, Mrad[a]	Atmosphere	Grafting yields at various monomer concentrations, %			
			20 vol.-%	40 vol.-%	60 vol.-%	80 vol.-%
Styrene	1	Vacuum	3	11	19	28
		Air	3	10	17	22
	5	Vacuum	27	61	74	89
		Air	30	68	75	104
	10	Vacuum	41	74	128	190
		Air	44	83	133	190
Methyl methacrylate	1	Vacuum	33	65	78	79
		Air	15	69	64	61
	5	Vacuum	16	30	39	46
		Air	24	30	31	42
	10	Vacuum	17	17	18	Lost[b]
		Air	17	16	12	Lost
Vinyl acetate	1	Vacuum	6	14	20	24
		Air	3	11	25	34
	5	Vacuum	9	18	26	Lost
		Air	9	21	29	35
	10	Vacuum	4	9	15	Lost
		Air	6	10	20	Lost

[a] Dose rate was 0.390 Mrad/hr.
[b] Strips were sometimes "lost" due to the insolubility of associated homopolymer.

The appearance of the Trommsdorff effect has been observed with other monomers (Tables II and V, Fig. 1), in particular with methyl methacrylate and 4-vinylpyridine. Again, the appearance of the maximum grafting rate for other monomers depends upon the type of monomer and solvent used and is also observed in both vacuum and air irradiations. In the grafting of styrene from homogeneous solution in dimethylformamide* (Fig. 1C), it is noteworthy that the increased grafting rate occurs at 35% monomer concentration, whereas this feature is absent at the lower total dose (Fig. 1E), where the maximum grafting rate in the system has not been attained.

Dose-Rate Effect

The presence of the Trommsdorff effect in cellulose grafting is evidently dose-rate dependent, as shown by the data of Figure 2 for styrene where the limiting dose rate for the effect appears to be approximately 0.25 Mrad/hr.

* It will be observed that this is the only instance where methanol has not been used as solvent in this paper. The data from dimethylformamide runs are included for comparison.

TABLE IV
Grafting with Vinyl Acetate in Methanol Solutions

Dose, Mrad	Dose rate, Mrad./hr.	Atmosphere	Grafting yields at various vinyl acetate concentrations, %			
			20 vol.-%	40 vol.-%	60 vol.-%	80 vol.-%
1	1.40	Vacuum	2	10	18	30
		Air	0	7	15	26
5		Vacuum	5	9	15	30
		Air	3	13	14	23
10		Vacuum	5	11	17	Lost[a]
		Air	5	10	17	Lost[a]
0.25	0.100	Vacuum	2	4	6	7
		Air	0	0	4	0
	0.250	Vacuum	0	2	3	4
		Air	0	1	3	5
	0.500	Vacuum	0	0	2	2
		Air	0	0	0	1
	0.750	Vacuum	0	1	2	2
		Air	0	0	0	0
0.5	0.100	Vacuum	0	6	7	7
		Air	0	1	8	—
	0.250	Vacuum	2	7	9	15
		Air	0	1	11	13
	0.500	Vacuum		4	8	8
		Air	0	2	8	13
	0.750	Vacuum	0	4	8	11
		Air	0	0	7	12
1	0.100	Vacuum	2	5	8	7
		Air	3	7	12	10
	0.250	Vacuum	4	11	17	15
		Air	3	9	15	19
	0.500	Vacuum	4	8	14	17
		Air	0	8	18	15
	0.750	Vacuum	2	8	11	13
		Air	0	3	16	20
0.5	0.796	Vacuum	4	9	12	14
		Air	4	8	16	24
0.25	0.215	Vacuum	3	5	9	6
		Air	3	3	5	8
		Vacuum	0	2	2	2
		Air[b]	0	0	0	2
0.5	0.215	Vacuum	4	7	11	12
		Air	4	5	10	13
		Vacuum	2	2	3	2
		Air[b]	2	3	2	3

[a] Strips were "lost" due to the formation of intractable and highly insoluble homopolymer.

[b] These strips had received a dose of 10^7 rad in air before use.

TABLE V
Grafting with Vinylpyridines in Methanol Solutions

Monomer	Dose, Mrad	Dose rate, Mrad/hr.	Atmosphere	Grafting yield at various solution concentrations, %[a]								
				10 vol.-%	20 vol.-%	30 vol.-%	40 vol.-%	50 vol.-%	60 vol.-%	70 vol.-%	80 vol.-%	90 vol.-%
4-Vinylpyridine	0.5	0.081	Air	2		23		27		21		11
4-Vinylpyridine	1	0.081	Air	12		28		41		72		20
4-Vinylpyridine	5[b]	0.145	Air		25		47		108		175	
2-Vinylpyridine	5[b]	0.145	Air		8		16		54		Insoluble mass	

[a] All strips were extracted in benzene, then in methanol to constant weight.
[b] These strips had been irradiated before use (2 Mrad at 0.150 Mrad/hr.) in air.

TABLE VI
Grafting by the Simultaneous Method to Preirradiated Cellulose

Dose rate, Mrad/hr.	Atmosphere	Total dose, Mrad	Grafting yields at various styrene concentrations, %[a]			
			20 vol.-%	40 vol.-%	60 vol.-%	80 vol.-%
0.390[b]	Vacuum	1	7(3)	20(10)	35(17)	38(26)
		5	44(26)	92(60)	94(70)	113(91)
		10	58(42)	106(79)	173(135)	218(200)
	Air	1	8(3)	20(10)	25(17)	30(20)
		5	52(30)	93(65)	99(74)	116(110)
		10	65(45)	110(84)	162(136)	228(197)
0.150[c]	Air	1	31(22)	55(49)	56(53)	61(59)

[a] The results in parenthesis are for the unirradiated control strips.

[b] These strips had received a dose of 10^7 rad in air before use. The results are mean values of duplicate determinations.

[c] These strips had received a dose of 10^6 rad in air before use. The results are mean values of quadruplicate determinations.

TABLE VII
Effects of Interrupted Irradiations[a]

Run no.	Irradiation conditions	Grafting yields at various monomer concentrations, %			
		20 vol.-%	35 vol.-%	60 vol.-%	80 vol.-%
1	Control	47	113	80	90
2	Interrupted dose[b]	51	129	96	117
3	Post-irradiation effect[c]	55	133	96	121

[a] Dose 1.5 Mrad in air at 0.145 Mrad/hr. using styrene–methanol solutions. Figures are mean values of five determinations.

[b] Three separate 0.5 Mrad doses given at periods of 3, 12, and 3 hr. between irradiations.

[c] These tubes allowed to stand for 170 hr. at room temperature before extraction.

for vacuum irradiations but only 0.14 Mrad/hr. for irradiations in air. Of more significance is the interrelationship between both total dose and dose rate, which function in parallel for the gel effect. The dose-rate effect for the irradiation of styrene in methanol, a poor solvent for the polymer, is also related to the monomer concentration, since at lower concentrations polymer is precipitated, whereas at the high concentrations coacervate formation may occur or the solution may remain homogeneous.

Qualitatively, it can be seen that as the dose increases the conversion of monomer progresses to the limit of solubility and, since the molecular weight of the polymer falls as the dose rate increases, the solubility of the polymer will be sustained, requiring larger doses to bring about precipitation. With certain combinations of dose, dose rate, and monomer concentration, swelling of polymer by the monomer may lead to the separation
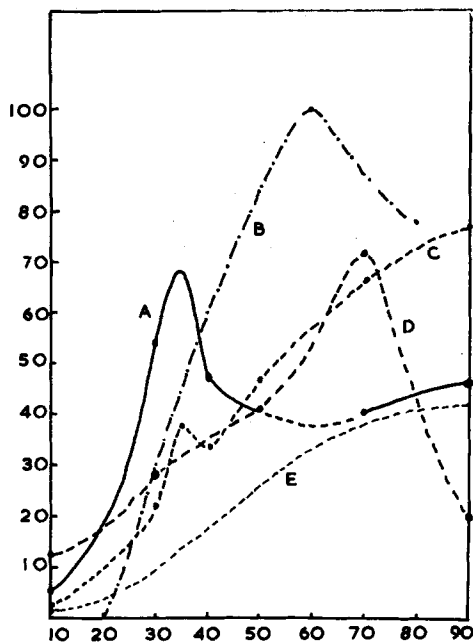
Fig. 1. Data showing maximum grafting rates for styrene, methyl methacrylate, and 4-vinylpyridine: (A) styrene in methanol, 1 Mrad in air at 0.077 Mrad/hr.; (B) methyl methacrylate in methanol, 0.18 Mrad in air at 0.045 Mrad/hr.; (C) styrene in dimethylformamide, 1 Mrad in air at 0.077 Mrad/hr.; (D) 4-vinylpyridine in methanol, 1 Mrad in air at 0.081 Mrad/hr.; (E) styrene in dimethylformamide, 0.5 Mrad in air at 0.077 Mrad/hr.

of a second liquid phase in the reaction mixture (Table VIII) rather than polymer precipitation. Grafting may then be erratic and dependent on reactions in one or other phase and the distribution of monomer in each.

Applied to the grafting process, the phenomenon depicted in the data of Table I may be dismissed as yet another manifestation of the Trommsdorff effect. There is no doubt that the effect operates in homogeneous solutions at high monomer concentrations. Here the increased viscosity and reduced mobility of the polymer chains lead to a reduction of the grafting rate. A direct consequence of the sustained homogeneity of the solutions is that the growing polystyrene chains do not become inactivated, so that the lengths of the grafted chains increase to give the high molecular weights usually associated with a reduced termination rate.

It is interesting, however, to speculate upon an alternative explanation functioning at low monomer concentrations where precipitation of the polymer occurs. In this case, it is possible that the continual removal of polymer and the burial of active radicals in the precipitated polymer, whether grafted or homopolymerized, favors grafting in a less restricted environment. It would be in the monomer concentration range of 30–35% that the grafting rate accelerates to this maximum value and, if such
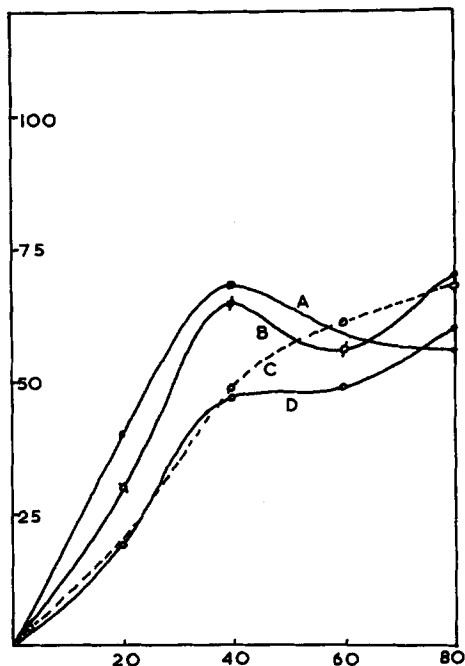
Fig. 2. Conditions which specify the appearance of maximum grafting rates (A) styrene–methanol solutions in vacuum, 1 Mrad at 0.140 Mrad/hr.; (B) styrene–methanol solutions in air, 1 Mrad at 0.140 Mrad/hr.; (C) styrene–methanol solutions in air, 1 Mrad at 0.250 Mrad/hr.; (D) styrene–methanol solutions in vacuum, 1 Mrad at 0.250 Mrad/hr.

a mechanism is valid, a simultaneous reduction in the molecular weights of the grafted chains is implied. This can only be consistent provided more extensive grafting along the cellulose chain takes place.

A fact which cannot be overlooked is that at high grafting yields, a preferential adsorption of monomer onto the grafted polymer would influence the reaction kinetics since $R_P > k_p$ [P·] [M]. Furthermore, this situation could arise during the course of the reaction. Here R_P is the grafting rate, k_p is the rate constant for propagation, [P·] and [M] are the concentrations of trunk radicals and monomer, respectively, illustrated for clarity in eqs. (1) and (2).

Initiation:

$$PX \rightarrow P\cdot + X\cdot \tag{1}$$

Propagation:

$$P\cdot + xM \rightarrow PM_x \tag{2}$$

Although the question of adsorption has not been examined in cellulose systems of this type, it is clear from the work of Odian et al.[17] from the swelling of nylon and polyethylene that the phenomenon can be of con-

TABLE VIII
Phase Separation During Grafting
from Styrene–Methanol Solutions

| Dose rate, Mrad/hr.	Monomer concentration, vol.-%	Dose, Mrad	Observation
0.668	20	1,5,10	Some polymer precipitation
	40	10	Nearly solid mass
	80	1	Increased viscosity only
	80	5,10	Two liquid phases form
0.39	20	1,5,10	Some polymer precipitation
	40	1	Some polymer precipitation
	40	5,10	Extensive precipitation, nearly solid
	60,80	1	Little change
	60,80	5,10	Precipitation of polymer, increasing with dose
0.14	20	1,5,10	Extensive precipitation, increasing with dose
	40	1,5,7.5	Greater precipitation of polymer than for 20% solution
	40	10	Solid mass
	60	5,7.5,10	Solid mass
	80	1	Appearance of droplets when irradiated in vacuum. Otherwise marked increase in viscosity only
	80	5,7.5,10	Solid mass
0.081	10,30	0.2	Some precipitation especially at lower concentration
	40,50,60,70	0.2	Homogeneous
0.0027	10,30	0.2	Precipitation of polymer
	50,70	0.2	Signs of precipitation
	80	0.2	Two liquid phases form

siderable importance. However, this may be vitiated by the finding[18] that polystyrene selectively adsorbs methanol from styrene–methanol mixtures containing more than 65% methanol. The importance of the adsorption phenomenon will be further discussed in the following charge-transfer theory treatment of grafting.[19]

Nature of the Graft Copolymer

No direct evidence for the existence of a chemical bond between cellulose and polystyrene has yet been obtained; however, the indirect results involving extraction, solubility, and molecular weight data support the concept of a chemical graft between the two entities. The nature of the actual type of bonding requires detailed comment as do the adsorption characteristics (briefly mentioned in the preceding section) of monomers in the irradiated cellulose system. In the opinion of the present authors, the two concepts may well be related. For bond formation to occur, the monomer (or polymer) and irradiated cellulose require to interact. Adsorp-

tion of monomer on irradiated cellulose certainly occurs in the system and would assist ultimate bond formation by lowering the initial energy of activation of the process. When cellulose in the form of paper etc. is irradiated with γ-rays, unpaired electrons will be formed, and these have been detected by electron spin resonance spectroscopy.[20-22] A reasonable proportion of these radical sites have lifetimes of years[20,21] and are generally inaccessible to molecules such as styrene and nitric oxide,[20,21,23] since the radicals effectively become a bulk property of the system. Those radicals which are accessible may form conventional bonds (grafts) with the monomer; however, other types of bonding are possible in this system and should be considered as sources of copolymerization. In the present interpretation, it is proposed that the "inaccessible" radical sites may still contribute to the ultimate bond formed in the graft if the bond is considered to be predominantly of a charge-transfer type. In the simplest example, styrene would be adsorbed to form a charge-transfer complex with the irradiated cellulose. The π-electrons of the styrene are considered to be delocalized during this process into the free valencies of the irradiated cellulose to form a stable charge-transfer bond. Analogous bonding is known in π-allylic inorganic complexes[24] and has been postulated for conventional aromatic substitution reactions.[25] Evidence is now accumulating to support the concept of π-complex adsorption on transition metals[26,27] and their oxides[28] in catalytic isotope exchange[26] and hydrogenation[29] reactions.

In applying the principle of charge-transfer complex formation to the present system, the monomer will be held or adsorbed in a flatwise position on the surface of the irradiated cellulose [eq. (3), where $\overset{.}{P}$ denotes a free radical either on the surface or within the cellulose].

$$2\overset{.}{P} + \langle\bigcirc\rangle\text{—CH=CH}_2 \longrightarrow \langle\bigcirc\rangle\text{—CH=CH}_2 \qquad (3)$$
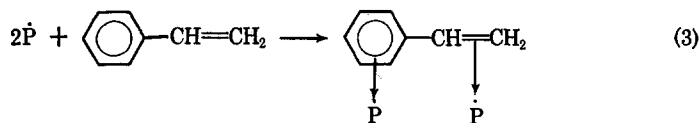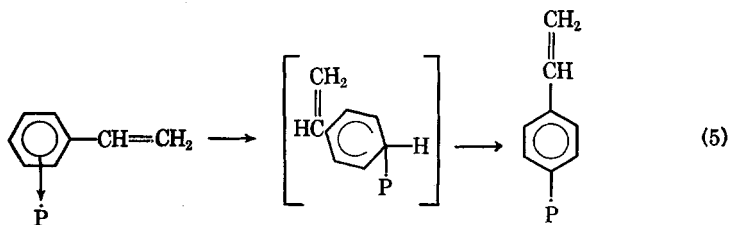
Two types of reactions may be involved, namely (1) radicals at the surface and (2) radicals in the bulk of the cellulose. In both examples π-bonding is possible, however, because of ease of accessibility of radical sites at the surface of the cellulose, further reaction may occur only in this instance to give a stable σ-bonded species, again similar to the π–σ bond conversion proposed for catalytic and inorganic systems.[30]

Grafting at the Surface. For simplicity, by considering the monomer styrene (or the polymer) and assuming in this case that the molecule is adsorbed as a π-complex through the aromatic ring π-electrons [eq. (4)], the horizontally adsorbed molecule may then react with an active site (P·) by a substitution reaction.
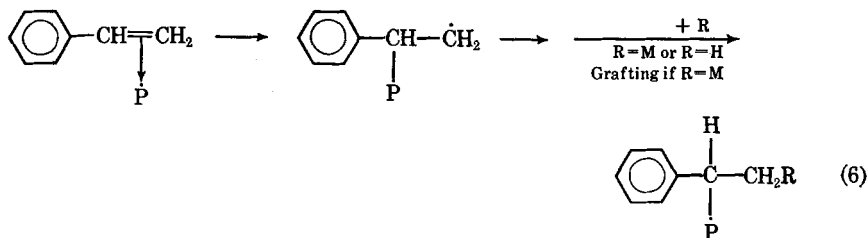
$$\langle\bigcirc\rangle\text{---CH}\text{==}CH_2 + \dot{P} \longrightarrow \langle\bigcirc\rangle\text{---CH}\text{==}CH_2 \qquad (4)$$

$$\downarrow$$
$$\dot{P}$$
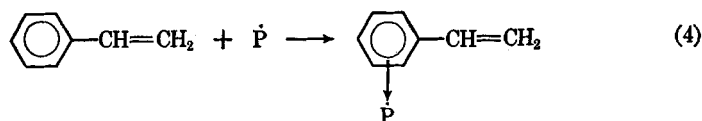
During this process it is proposed that the molecule rotates through 90° and changes from horizontal π-complex adsorption to the vertical σ-bonded state [eq. (5)]. Rotation of the ring is necessary since "edge-on" or "vertical" π-complexing is

$$\langle\bigcirc\rangle\text{---CH}\text{==}CH_2 \longrightarrow \left[\begin{array}{c} CH_2 \\ \| \\ HC\langle\bigcirc\rangle\text{---H} \\ P \end{array} \right] \longrightarrow \begin{array}{c} CH_2 \\ \| \\ CH \\ \bigcirc \\ \dot{P} \end{array} \qquad (5)$$
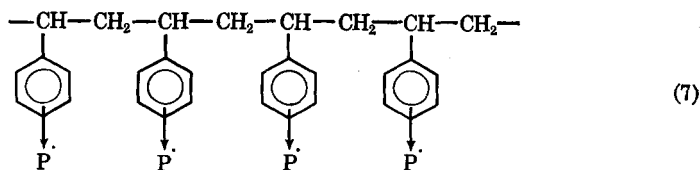
prevented by orbital symmetry and by the steric hindrance of aromatic hydrogen atoms. It is postulated that the transition state of the π–σ bond conversion occurs approximately when the plane of the rotating aromatic molecule is at an angle of 45° to the cellulose surface.

An analogous mechanism may also be proposed to show π-bonding through the side-chain group [eq. (6)].

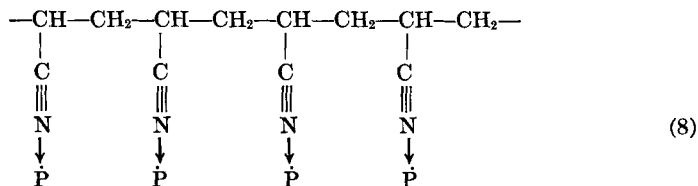$$\langle\bigcirc\rangle\text{---CH}\text{==}CH_2 \longrightarrow \langle\bigcirc\rangle\text{---CH}\text{---}\dot{C}H_2 \longrightarrow \underset{\substack{R=M \text{ or } R=H \\ \text{Grafting if } R=M}}{\xrightarrow{+R}}$$

$$\downarrow \qquad\qquad\qquad \downarrow$$
$$\dot{P} \qquad\qquad\qquad P$$

$$\begin{array}{c} H \\ | \\ \langle\bigcirc\rangle\text{---}C\text{---}CH_2R \\ | \\ \dot{P} \end{array} \qquad (6)$$

Grafting in Bulk. In this instance mobility of polystyrene chains and radicals would be impeded and a mechanism analogous to the π–σ conversion already proposed would be difficult to apply because of the physical limitations of the system. However, a modified form of eq. (4) may be envisaged, particularly if long polystyrene chains are involved. These chains could be held by a series of charge-transfer bonds as illustrated by eq. (7).

$$\text{---CH---}CH_2\text{---CH---}CH_2\text{---CH---}CH_2\text{---CH---}CH_2\text{---}$$

$$\bigcirc \qquad \bigcirc \qquad \bigcirc \qquad \bigcirc \qquad\qquad (7)$$

$$\dot{P} \qquad \dot{P} \qquad \dot{P} \qquad \dot{P}$$

Bonding of this type would be extremely strong and would tend to keep some homopolymer locked between the chains as "graft" polymer. In terms of this mechanism, one could distinguish between two types of grafts (a) σ-bonded at the surface, presumably in low concentration and (b) essentially π-bonded within the bulk of the cellulose.

This proposed model would explain apparent anomalies observed with the extraction of homopolymers from copolymerized celluloses using hot solvents. The model is also applicable to grafting initiated by ultraviolet radiation[31] and ceric ions.[32, 33] It may also explain the role of methanol, which is known to adsorb strongly on surfaces and to displace water,[34] thus making available cellulose sites for graft formation.

The charge-transfer mechanism may also be used to interpret bonding involving radiation-induced grafts between cellulose and monomers other than styrene, e.g., acrylonitrile, methyl methacrylate, etc. In the case of such monomers, it would be anticipated that the functional group would act as the donor for charge-transfer bonding in the bulk as shown in eq. (8).

$$
\begin{array}{cccc}
-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2- \\
| \qquad\qquad | \qquad\qquad | \qquad\qquad | \\
\text{C} \qquad\quad \text{C} \qquad\quad \text{C} \qquad\quad \text{C} \\
\| \| \| \qquad \| \| \| \qquad \| \| \| \qquad \| \| \| \\
\text{N} \qquad\quad \text{N} \qquad\quad \text{N} \qquad\quad \text{N} \\
\downarrow \qquad\quad \downarrow \qquad\quad \downarrow \qquad\quad \downarrow \\
\text{P} \qquad\quad \text{P} \qquad\quad \text{P} \qquad\quad \text{P}
\end{array} \qquad (8)
$$

Under these circumstances such bonding would not be as strong as the bonding from an aromatic ring as with styrene [eq. (7)], and this may be one of the essential reasons why styrene has proved to be the most satisfactory of the monomers studied for the present radiation-induced grafting experiments.

In conclusion, we wish to stress again that in our opinion bonding in the present system may not occur exclusively by the charge-transfer mechanism, although this concept has many attractive features and may well be the predominant mechanism involved in the radiation grafting process. This interpretation has the added advantage of being generally applicable to other trunk polymers.

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Résumé

Le greffage induit par irradiation de la cellulose au moyen de styrène, de méthacrylate de méthyle, d'acétate de vinyle et des 4-vinylpyridines dans le méthanol a été étudié. Tous ces monomères montrent un greffage appréciable à température de chambre aussi bien sous vide qu'à l'air pour des doses totales allant jusqu'à 10 Mrads et à des vitesses de

dose aussi élevées que 1.4 Mrad/hr. dans un réacteur habituel.   La grandeur du greffage dépend à la fois de la dose totale et de la vitesse de dose.   Dans des conditions expéri-mentales déterminées, les expériences de greffage montrent un maximum qui a été at-tribué à l'effet de Trommsdorff.   Un mécanisme nouveau comportant la formation d'un lien par transfert de charge est proposé en vue de rendre compte des effets observés au cours des réactions de greffage.

Zusammenfassung

Die strahlungsinduzierte Aufpfropfung von Styrol, Methylmethacrylat, Vinylacetat, 2- und 4-Vinylpyridin auf Cellulose in Methanol wurde untersucht.   Alle Monomeren zeigen beträchtliche Aufpfropfung bei Raumtemperatur in Vakuum oder in Luft bei Gesamtdosen bis zu 10 Mrad und Dosisleistungen bis zur Höhe von 1,4 Mrad/h in einem erschöpften Brennelement oder einer Cobalt-60-Quelle.   Die Grösse der Aufpfropfung hängt von Gesamtdosis und Dosisleistung ab.   Unter gewissen Bedingungen tritt ein Pfropfungsmaximum auf, das auf den Trommsdorff-Effekt zurückgeführt wird.   Zur Erklärung der Befunde bei den Pfropfreaktionen wird ein neuartiger Mechanismus mit Bildung von Ladung-Ubertratungsbindungen angegeben.